

“Variations in the Electromotive Force of Clark Cells with Temperature.” By W. E. AYRTON, F.R.S., and W. R. COOPER, M.A., B.Sc. Received October 29,—Read December 5, 1895.

The present position of the Clark cell as a standard of E.M.F. is one of such great importance that it is highly desirable to study its behaviour under all working conditions. From time to time during the last few years the Board of Trade has issued specifications relating to its preparation, each one of which was modified according to the results obtained by the use of the one that preceded it. This led finally to the adoption of the cell as a standard, the specification being included in an Order in Council of last year. More recently, in a slightly different form, it has been legally adopted by the United States of America, and it is probable that other countries will soon follow in the adoption of a standard which may already be regarded as universal.

In this paper we propose to deal with temperature variations and their effect upon the accuracy of this standard.

When employing a Clark cell for electrical measurements, it is often difficult to avoid changes of temperature which are sufficient to cause appreciable error if a corresponding correction is not applied. For example, in comparing such cells between themselves at frequent intervals, the differences are generally observed to change from test to test, and, in order that the figures obtained may be of any value, it is of some importance to know how readily variations of temperature are reproduced as variations of E.M.F. in any particular cell. It is very usual to assume that the temperature coefficient amounts approximately to 0·077 per cent. per degree Centigrade, or that the E.M.F. is diminished by 0·0011 volt per degree rise of temperature. There is no doubt that such is often the case, at least for considerable changes of temperature at a slow rate. But we have always felt that a good deal of uncertainty might exist as to the extent of this correction, according as the temperature variation is very slow or comparatively rapid. Of course, large variations of temperature would always be avoided, as they must necessarily be accompanied by a lag in the corresponding changes of E.M.F.; but, although ordinary precautions may be taken, small variations generally occur.

The question then arises—Are we justified in applying in full the correction given above for variations of temperature such as occur in practice, or should its value be materially diminished, except when the cells have been subsequently kept at a steady temperature for a very considerable time. It was with a view of obtaining more definite

information upon this matter than could be found in any work upon the subject that the experiments described below were begun more than two years ago. It also appeared desirable to ascertain to what degree of accuracy temperature coefficients could be determined by observing the changes in E.M.F. during a continuous change of temperature.

The tests were in all cases carried out upon cells set up in accordance with the specifications of the Board of Trade, the greater number of the cells employed in the investigation having been constructed by one of the authors. Those employed in the preliminary experiments were set up according to the specification of October, 1892, but the remainder were made according to the final specification of the Board of Trade. They were contained in what are known as "sample tubes," approximately 1 inch in diameter, and the quantity of paste and mercury employed was not large, the figures given in the instructions being adhered to as far as possible. It will be readily understood that many of the results obtained only hold good for this class of cell, and that there might be considerable modifications introduced by any large increase or decrease in the size of the cell.

The method in the preliminary experiments was somewhat approximate. Current from a storage cell, in series with a resistance, traversed a potentiometer wire, the resistance being such that the fall of potential along the wire amounted to either one ten-thousandth or one five-thousandth of a volt per centimetre length as required. The E.M.F. of the storage cell was observed at intervals, so that any necessary correction might be applied, and the current could be reversed at any time by means of a key. The cell to be tested was joined up in opposition to the standard, and their difference in E.M.F. at once determined by the method of compensation.

The standard used in the comparison consisted of one or other of three Clark cells, kept, as far as possible, at a constant temperature, ice being employed for that purpose. The cells were placed in corked boiling tubes, and these were supported in a water bath. The latter was packed round with cotton wool in a wooden case, the lid of which was only removed to replenish the bath with ice. Radiation was thus diminished to a great extent, and as these preliminary experiments were carried on during the winter it was possible to maintain a comparatively low temperature in the room itself. Nevertheless, variations of half a degree, or more, often occurred in this preliminary investigation, and the bath was considerably warmer at the bottom than at the top. It was found best to pack a large amount of ice into the bath, so that this difference remained fairly constant. In general it amounted to about 1.5°C . As it was difficult to apply a satisfactory correction, any variations in the temperature of the bath had to be neglected. One of the above cells was employed

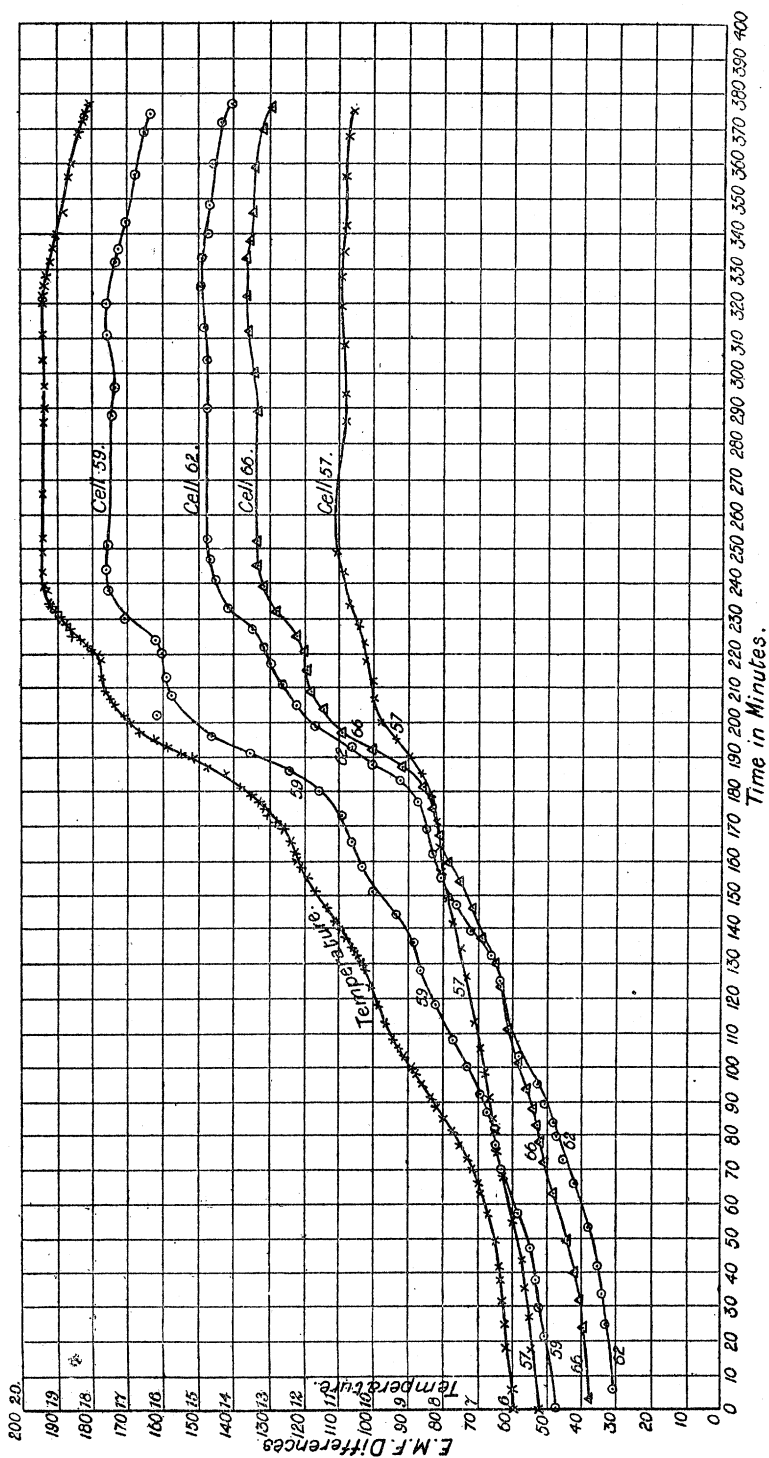
throughout for balancing the cells under test, and it was compared at frequent intervals with the other two in the ice bath. The differences between these were remarkably constant, so that it was probable that the standard did not change to any great extent.

Experiments were conducted upon several cells at a time. These were placed in a water bath surrounded by an outer vessel, also containing water. Heat was applied, and time readings were taken of the temperature of the inner bath and of the differences of E.M.F. between each cell and the standard. The initial temperature was always that of the room, and, as there was an interval of at least one night between successive experiments, the cells were presumably in a fairly steady state before any heating began. The results were plotted in the form of curves, some of which are reproduced, having time as abscissæ, and temperature, or variations of E.M.F., as ordinates. In fig. 1 is shown the effect on four cells of a rise of 13.4° C. in about four hours, after which the temperature was maintained approximately constant for nearly one hour and a half, and then allowed to slowly fall. The upper curve shows exactly how the temperature was changing at any time; and the lower curves the corresponding effect on the E.M.F. of each of the cells. It will be seen that each of the latter is similar to the temperature curve, the irregularities of which are reproduced more or less closely according to the sensitiveness of the cell. All the lower curves are, however, displaced somewhat to the right, compared with the temperature; that is, a change of curvature, or a maximum in E.M.F., is generally reproduced somewhat later than it occurs in the temperature curve. There is, in fact, as would be expected for such a rate of variation of temperature, a lag which is not the same in value for all the cells. It will be observed that every cell curve drops almost as soon as the temperature begins to fall.

These preliminary experiments all tended to show that cells responded very readily to variations of temperature. In fact, a glance at the curves would lead one to think that lag was negligible, and that cells reached a practically steady state after a few minutes of steady temperature, any further small changes of the latter being reproduced without delay. But these results can only be regarded as approximate, and leave out of the question any possibility of what may be termed a *semi-permanent lag*, by which we mean any slow settling down after a large variation of temperature, before a cell attains a really steady condition. It, therefore, appeared desirable to carry out further experiments with increased precautions to ensure accuracy.

For this purpose three cells were again used as a standard, and were placed in boiling tubes fixed in a water bath, but instead of putting ice into the latter it was surrounded by an outer vessel into

Fig. 1.

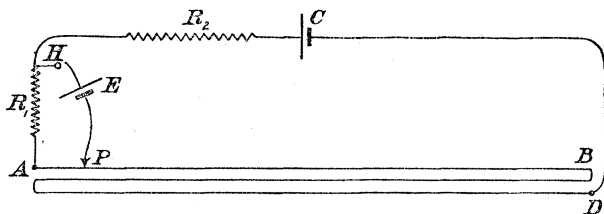


which ice could be packed. As the ice melted the water was carried off by a tube so that it stood at a level slightly above the bottom of the inner bath. The whole was surrounded by cotton-wool in a wooden case. By filling the outer bath with ice every evening it was found possible to maintain the temperature of the inner bath fairly constant throughout the following day, the variation rarely exceeding two or three-tenths of a degree in the hottest weather.

In order to check any variation of the standard through causes other than temperature, it was frequently balanced against the P. D. due to a known current of about $\frac{1}{2}$ ampere passing through a known resistance of about 3 ohms. The latter was made especially for the purpose, of manganin wire, wound upon an ebonite frame and immersed in paraffin oil. It was previously aged by heating for five hours at 140°C ., and it assumed a steady value after two or three weeks, as shown by frequent comparisons with standard manganin coils. The current was measured by a Kelvin centiampere balance, the constant of which had frequently been checked by means of a silver voltameter. By this means a variation of 0.00015 volt could be detected without difficulty.

The standards were soon found to become remarkably constant in value. The E.M.F. of one cell was tested absolutely, as above described, before and after every experiment, and the three cells were also frequently compared during the course of an experiment. The results were very consistent.

FIG. 2.



A stretched wire, ABD (fig. 2), 3 metres in length, was employed in comparing cells under test. The resistance of this being known, the strength of current necessary to give a drop of potential of one ten-thousandth of a volt per half centimetre length was calculated, and also the resistance required when traversed by this current to balance one of the standards whose E.M.F. was known. The resistance R_1 in the diagram was adjusted so as to be as nearly up to this value as possible, and the deficit was found in terms of a length AP of the stretched wire. For example, suppose the resistance necessary to balance the E.M.F. of the standard cell E was found by calculation to

be 107.15 ohms. Plugs would be taken out of the box R_1 to the value of 107 ohms, and the point P on the wire would be selected such that AP equalled 0.15 ohm. The current through the wire supplied by a storage cell, C, was then adjusted by the auxiliary resistance R_2 until the standard E was balanced between the points H and P, or so nearly balanced that no appreciable error would result. In this way the wire was rendered direct reading for any subsequent comparisons, $\frac{1}{2}$ cm. on the scale corresponding with one ten-thousandth of a volt. A mercury cup was attached to the terminal of R_1 ; it was therefore possible to join E with the end of R_1 by simply dipping a wire into the mercury. Thus, any change of resistance in the main circuit by different pressure of the terminal, &c., was eliminated, and the value of the current could be readily checked at any time without interrupting the main circuit. This was done at frequent intervals throughout every experiment. As a rule, very little variation was found to take place. The value of the E.M.F. of the standard cell was, of course, previously known by an absolute determination.

The cells under test were always connected with the point B of the wire (1 metre from A), and were balanced against the standard with never less than 10,000 ohms in series. The cells were placed in a water bath, having room for five; the positive poles were joined to a common terminal, the negatives being led to separate mercury cups. Two stirrers were provided for keeping the temperature of the water uniform. There was also an outer bath containing the bath just mentioned. This outer one was heated when required by passing steam through a piece of tubing immersed in the water, and cooled when necessary by means of ice.

The temperature of a set of cells was generally varied through a considerable range, and brought back to practically the same value as it had at the beginning of the experiment. Supposing no lag to exist, the curve connecting temperature and E.M.F. would be the same for both rising and falling temperature. But if there is a lag of short duration (*i.e.*, not cumulative), then, provided that the temperature varies at the same rate throughout, two distinct curves, parallel to the first for the greater part of their length, will result, and will enclose an area between them.

Further, if there is any *semi-permanent lag*, cumulative in its character, the form of curve shown at *pq* (fig. 3) would result, the up and down curves being parallel to one another, but inclined to the true direction *pq*.* This assumes that the lag has the same value

* When the temperature rises the E.M.F. falls and the E.M.F. differences increase. In all curves between temperature and E.M.F. differences the axis relating to the latter has therefore been drawn downwards. The origin for E.M.F. is of course at a different point from that for E.M.F. differences, but the former is

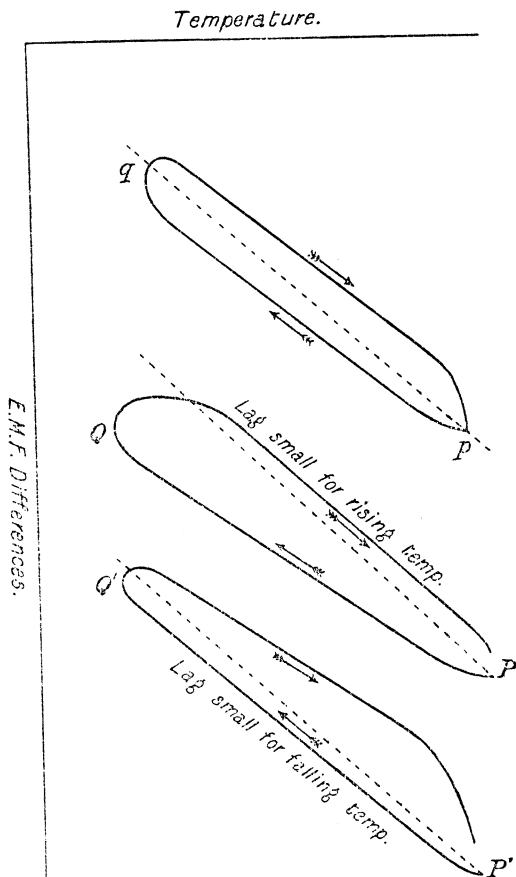


FIG. 3.—Temperature first falling and then rising.

for both rising and falling temperature, and that the range is sufficiently extensive for the conclusion of the experiment to be unaffected by the lag due to the first slope of temperature.

But if the lag has a different value for rising and falling temperature, the shape of the curve will be different. Suppose the temperature to be first lowered; then if the lag is large for a falling and small for a rising temperature, a curve of the form PQ, starting from P, fig. 3, will result, the falling curve PQ (by which we mean the curve for falling temperature) diverging considerably from the

often employed loosely for the latter, for the sake of brevity in descriptions. Observations with falling temperature are marked on these curves thus—($\times$), and with rising thus—($\odot$). All differences of E.M.F. are expressed in ten-thousandths of a volt and temperature in degrees Centigrade.

normal direction, shown by the dotted line. The rising curve, on the other hand, will be nearly parallel to it. But if the lag is small for a falling and large for a rising temperature, a curve of the form $P'Q'$, fig. 3, will result, the falling curve $P'Q'$ having nearly the normal direction, while the rising curve will diverge to a much greater extent.

Similar curves will be obtained when the temperature is instead first raised and then lowered. If the lag is larger for falling than for rising temperature, a curve of the form PQ , fig. 4, will result, wider near the starting point P than at the other end, whereas if the converse is the case the curve will be of the form $P'Q'$, narrower near the starting point than at higher temperatures.

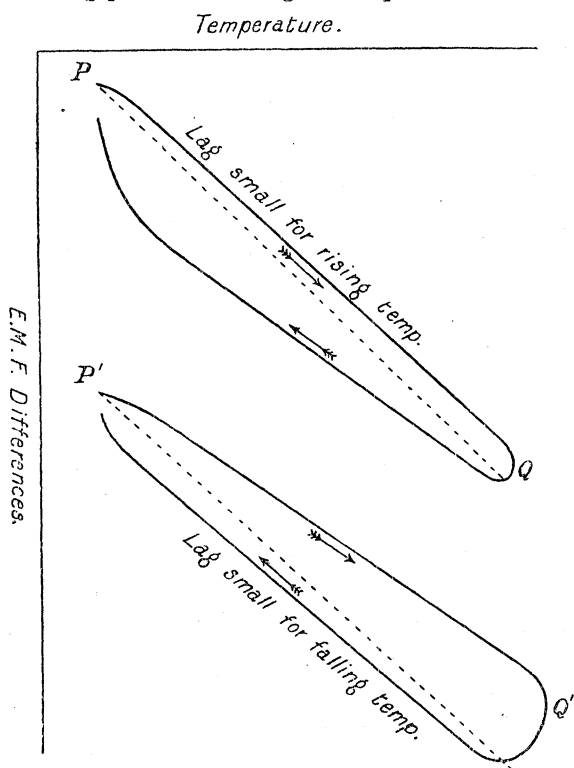


FIG. 4.—Temperature first rising and then falling.

Any lag of the ordinary kind will soon pass off after a steady temperature is reached, or after the temperature gradient is reversed. But any lag of a semi-permanent character will prevent the curve from returning to its starting point until after the lapse of a considerable time, and will thus produce a break.

In order to investigate the matter, several cells were subjected to such cycles of temperature. For the results to be of any value it was necessary that the temperature should be varied uniformly, and preferably at the same rate when both rising and falling. A good deal of difficulty was at first experienced, but some excellent temperature curves were afterwards obtained by Mr. W. G. Rhodes, to whom we are much indebted for assistance rendered throughout this tedious part of the work. If the temperature slope became seriously irregular it was readily detected upon plotting the curve of temperature and time, and the E.M.F. readings corresponding with any such irregular periods were then neglected in plotting the curves between the temperature and E.M.F.

The curves for E.M.F. differences that are reproduced should be considered along with the corresponding temperature curves, which in all cases are drawn underneath the former. Rather a large selection is given so as to avoid the formation of any erroneous conclusion. It will be noticed that the parts of an E.M.F. difference curve relating to rising and falling temperature are seldom parallel. It might be urged that this is due to residual changes of temperature making themselves felt on the return curve. But all our experiments tend to show that lag (excluding semi-permanent lag) for this rate of variation of temperature does not, as a rule, exceed a quarter of an hour. The curves at either end would be affected in this manner for a length corresponding with about one degree (the rate of variation being about one degree every quarter of an hour). Beyond that errors might arise amounting to one, or two, ten-thousandths of a volt, due to semi-permanent lag, but they would be insufficient to change the general character of the curves.

In order to avoid confusion, the cell curves have been separated when necessary by displacing the origin of E.M.F. differences, so that different sets of figures along this axis correspond with different cells, as shown by the distinguishing letters above them. It must be remembered that all the cells included in any one diagram were subjected to *precisely* the same treatment and tested under *precisely* the same conditions.

These curves indicate that the lag has generally a different value for rising and falling temperature. The curves in fig. 5 were obtained by lowering the temperature about 9.5° , and then raising it through the same range, but somewhat more rapidly. The lag appears to be smaller for a rising temperature in the case of cells B, M, and L, the difference being but slight in the last. Cells G and N are practically neutral in this respect, although it is to be observed that all the cells were in the same bath.

The curves in fig. 6 were obtained by lowering the temperature

FIG. 5.

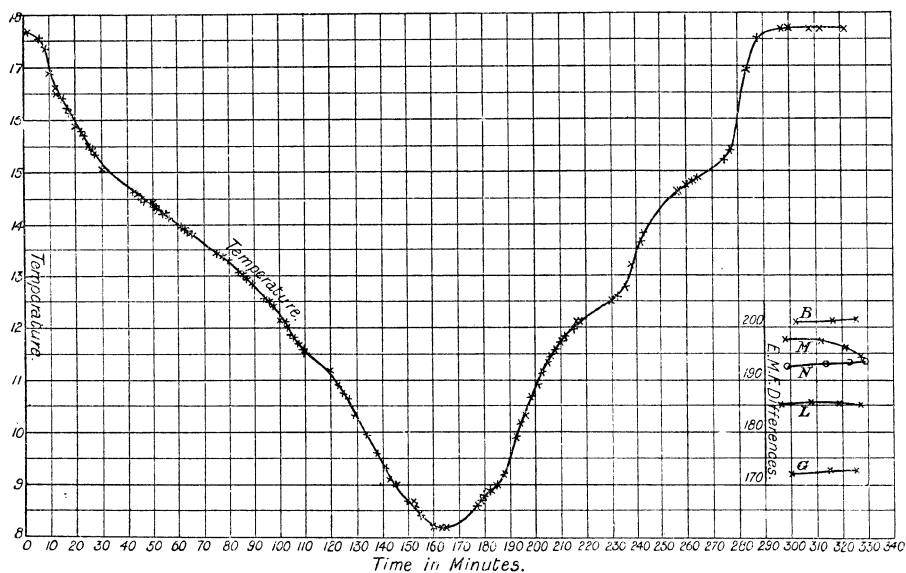
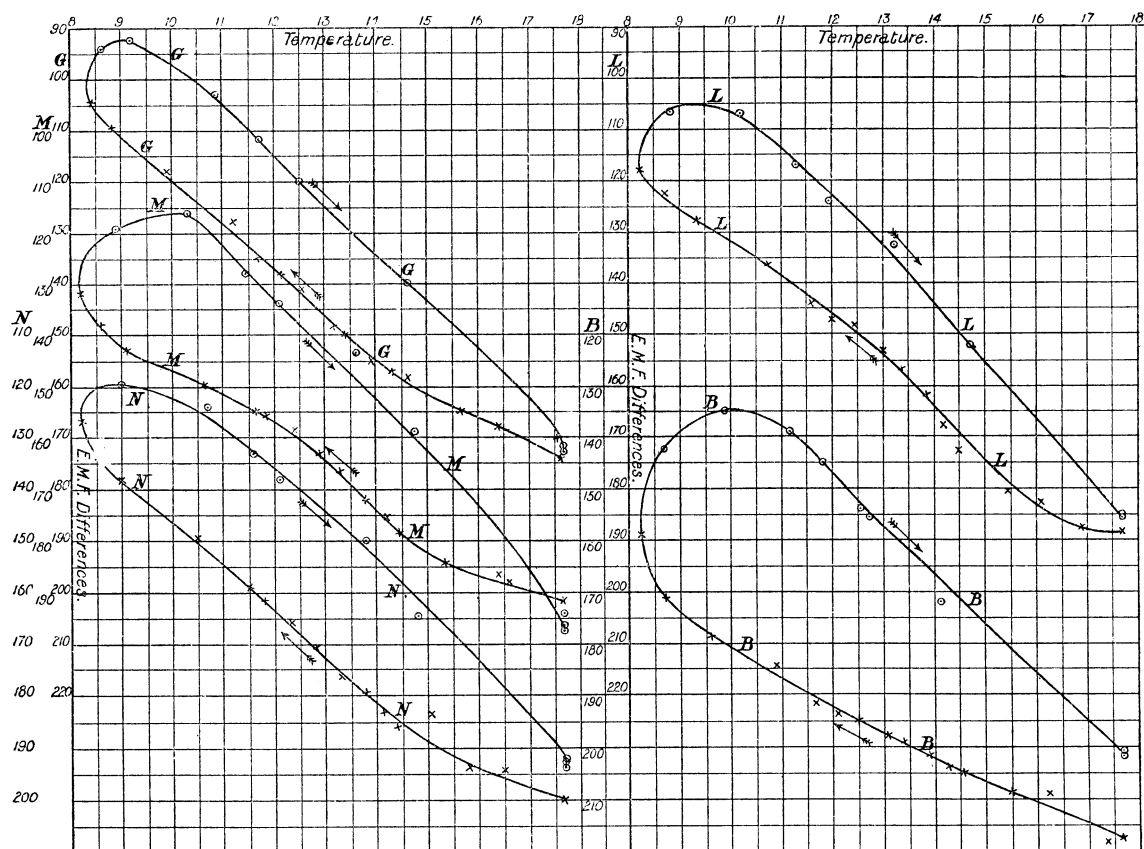


FIG. 6.

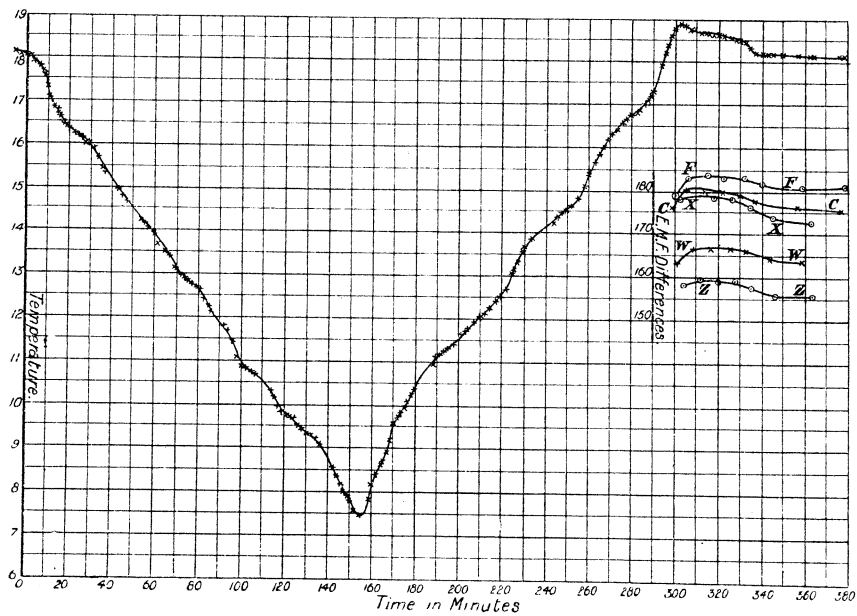
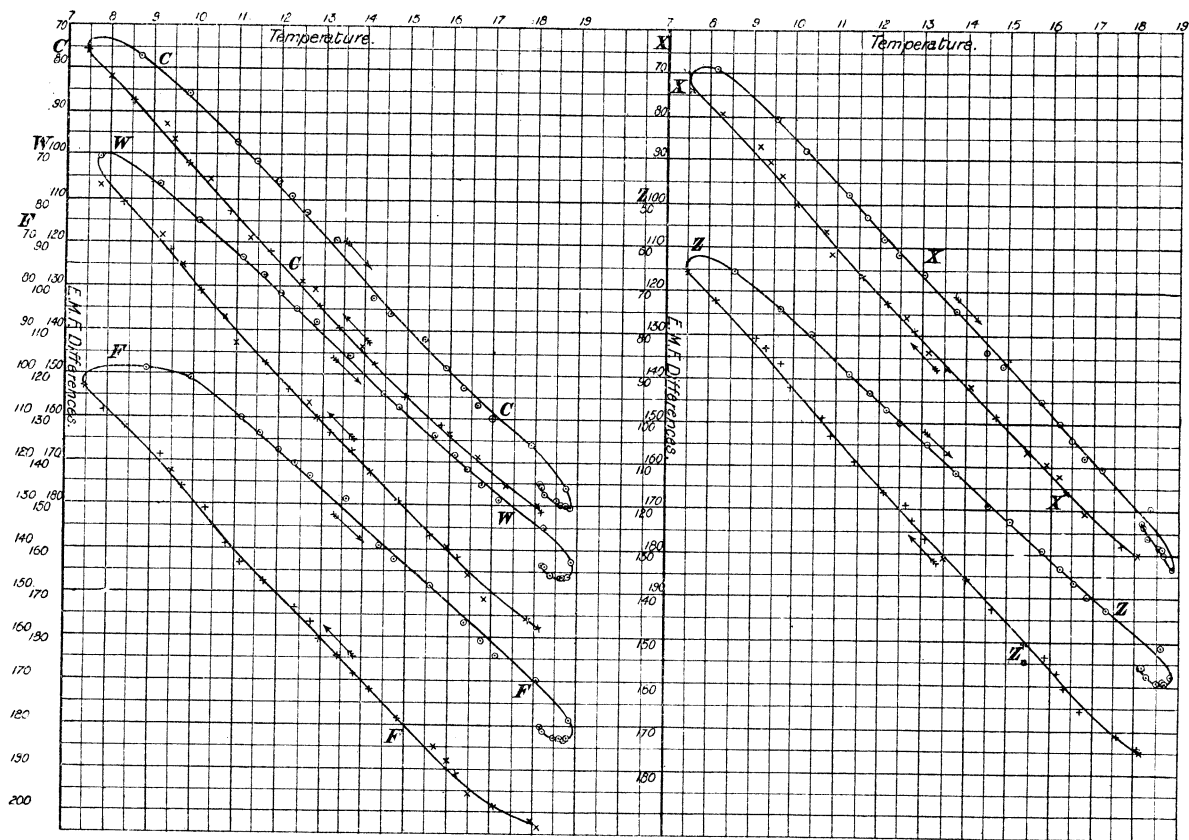


Fig. 7.

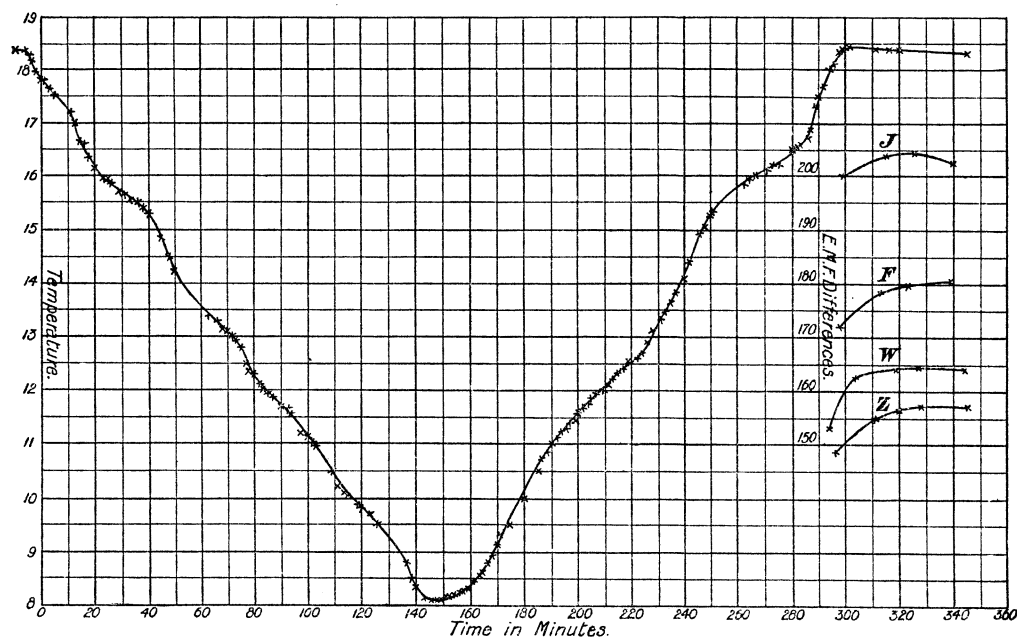
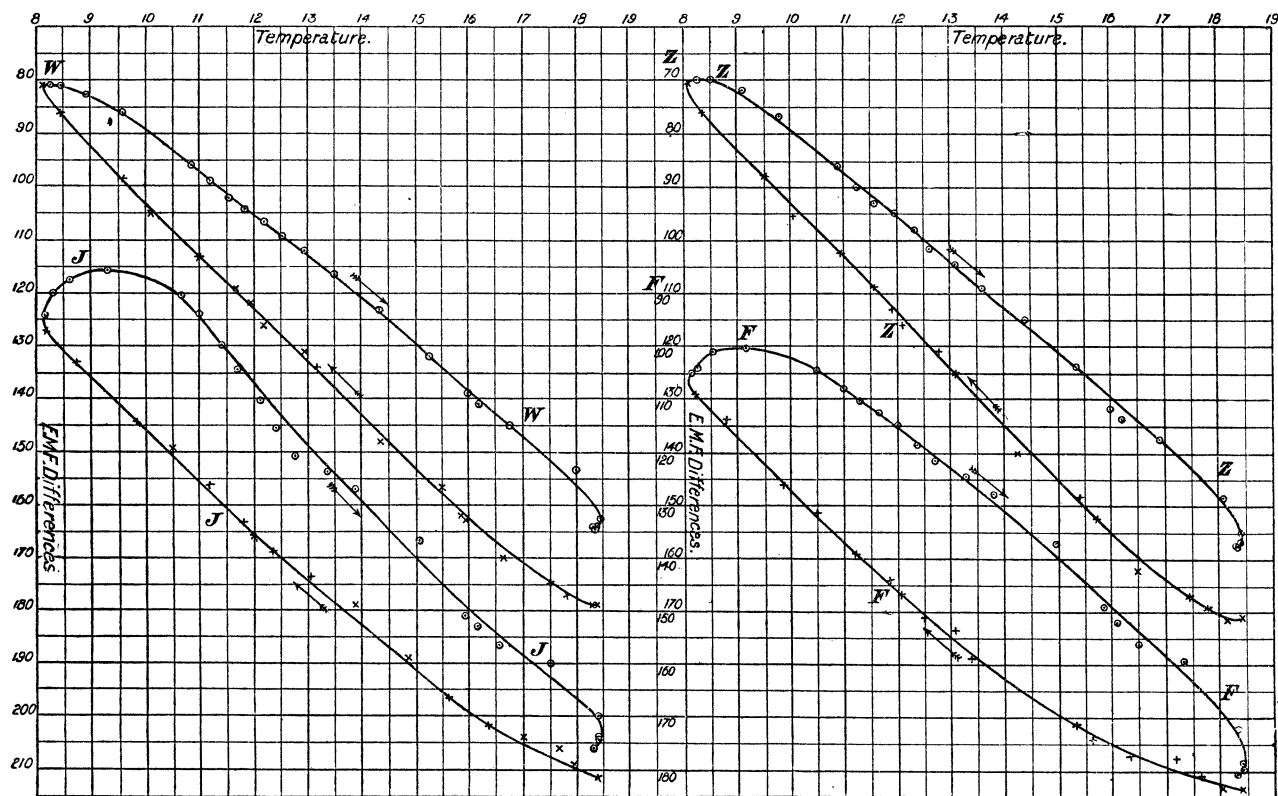
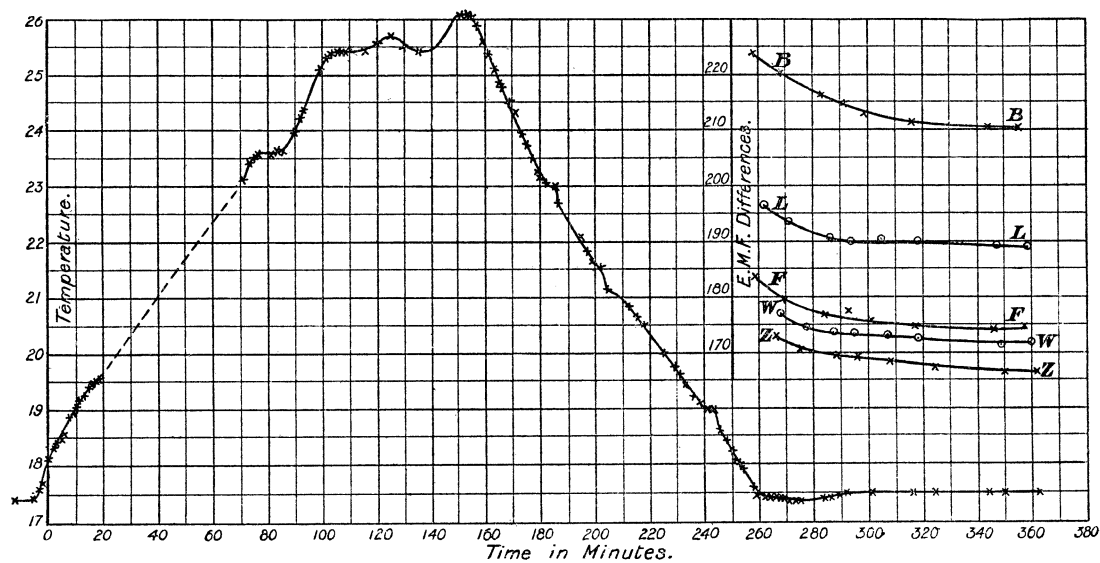
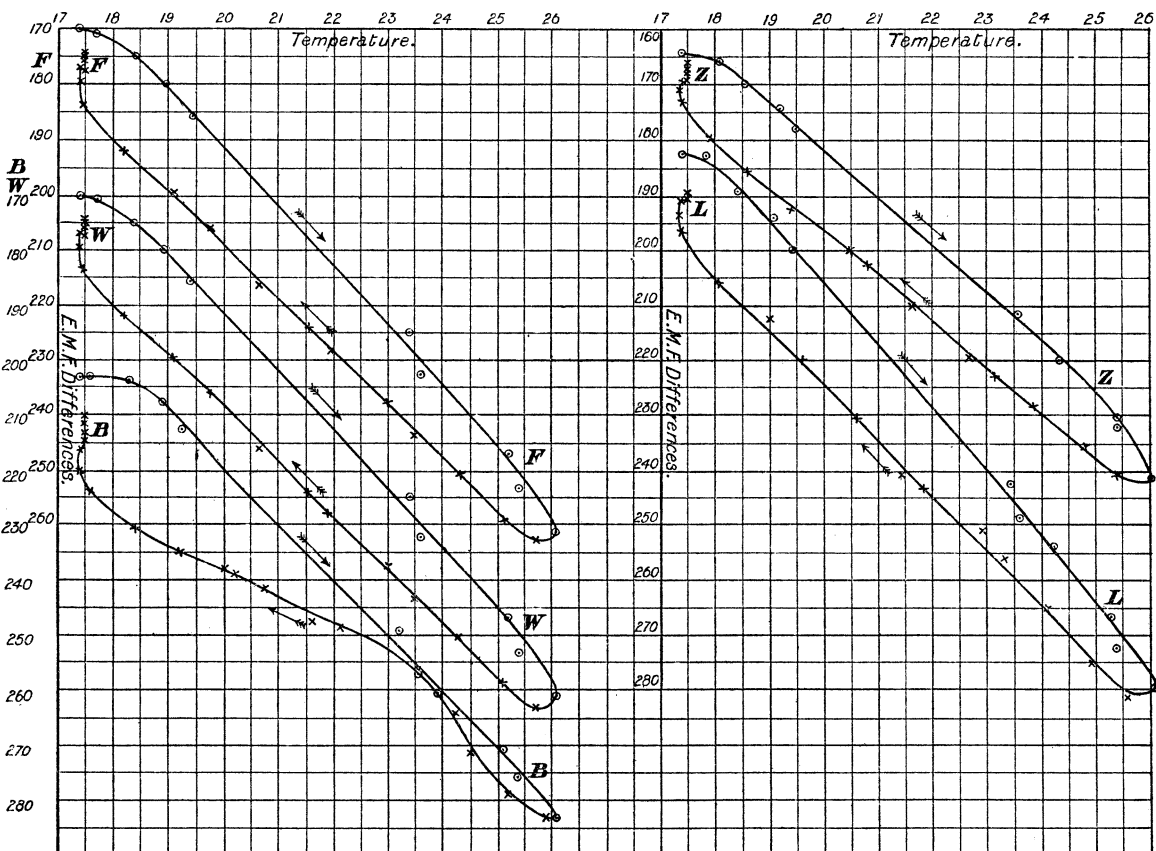


FIG. 8.



about $10\cdot5^{\circ}$, and raising it again at the rate of one degree every quarter of an hour. Cells F, W, and Z appear to have a smaller lag with a falling than with a rising temperature, whereas there is very little difference in cells C and X. In fig. 7 curves are shown for nearly the same range of temperature, but this was maintained for a longer time near its lowest point. Cells W and Z give curves similar to those in fig. 6. J has a smaller lag for rising temperature, and F appears neutral, though enclosing a large area. Fig. 8 shows curves obtained when the temperature was first *raised* and then lowered through about $8\cdot5^{\circ}$ at the rate of one degree per quarter of an hour. Unfortunately we were accidentally prevented from taking observations during one part of the time, but there is little doubt that the curves follow pretty nearly the course marked. It is noticeable that cells F and perhaps W appear to have a slightly smaller lag with a rising than with a falling temperature, whereas the reverse is the case in figures 6 and 7. Cell L has a similar curve, and Z is now neutral, though not so formerly. Inequality of lag for rising and falling temperature thus appears to vary from cell to cell, and even to vary largely in any one cell, as shown by the curves for cell B and others. The following table gives these results in a manner more easy for comparison:—

Conditions of experiment.	Lag smaller for rising temperature.	Neutral.	Lag smaller for falling temperature.
Fig. 5. Fall and rise through $9\cdot5^{\circ}$	B, L (slight), M	G, N	
Fig. 6. " " $10\cdot5^{\circ}$	..	C, X	F, W, Z
Fig. 7. " " $10\cdot0^{\circ}$	J	F	W, Z
Fig. 8. Rise and fall through $8\cdot5^{\circ}$	B, F (slight), L (slight), W (?)	Z	
Fig. 9. " " $2\cdot0^{\circ}$	F, L	W, Z	

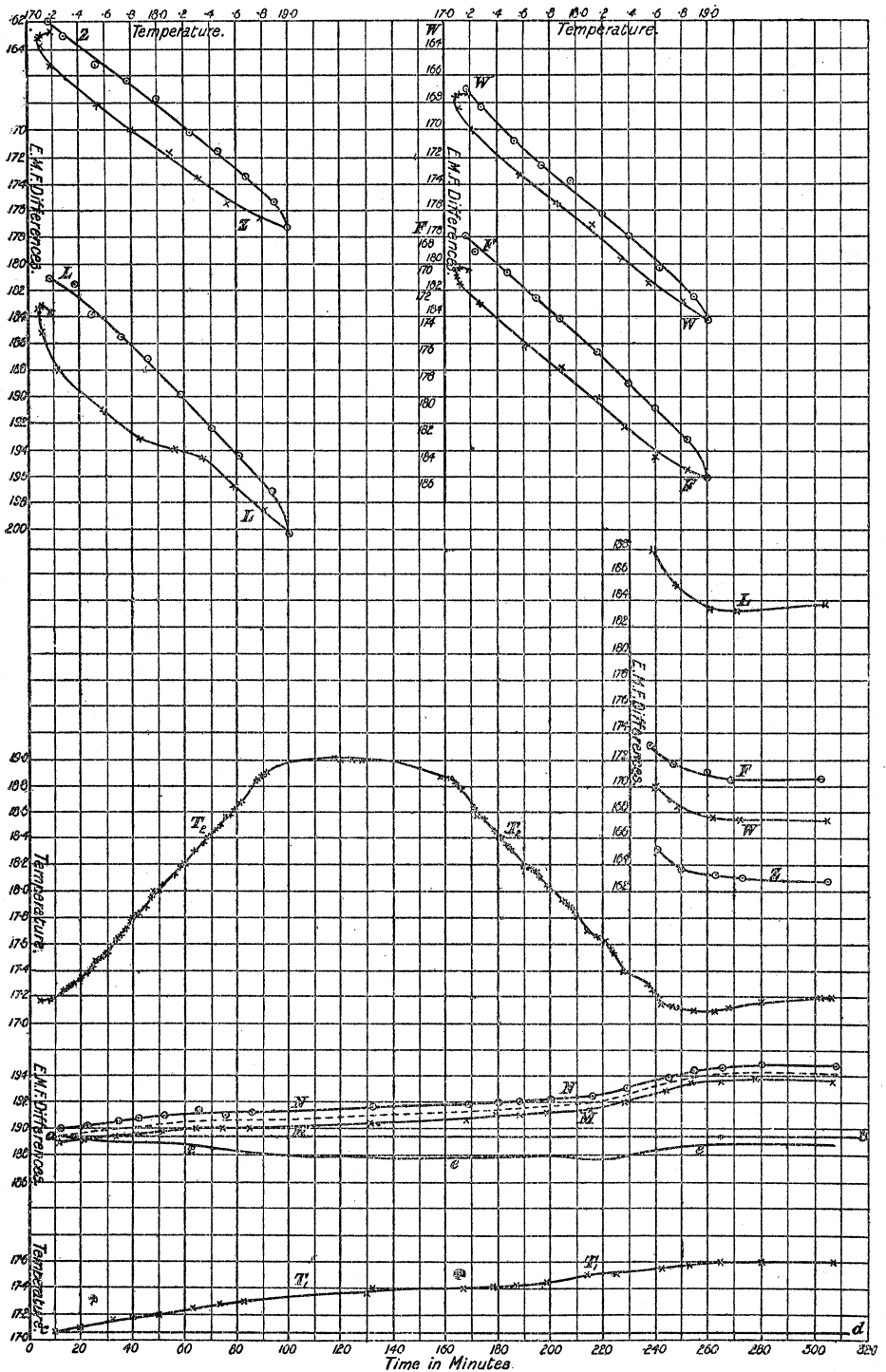
It will also be observed that the curves between temperature and E.M.F. are seldom closed, even though readings were continued for some time after the former assumed a steady value, as may be seen by referring to the curves relating to temperature alone. At the end of any experiment the cells became practically steady after about twenty minutes, and would then readily follow any subsequent variations, as, for example, in fig. 6. The slow rate at which cells assume a really steady state is shown by the curves which have been plotted between E.M.F. differences and time in the lower right-hand corner of figs. 5, 6, 7, 8, and which refer to the conclusion of each experiment. One hour and a half is generally quite insufficient to remove the semi-permanent lag for this rate of variation, as shown in fig. 8;

indeed, it is sometimes found not to have completely disappeared by the next morning. In extent it seems to vary considerably, even in the same cell. For example, in the cell F, it is large in fig. 6, small in fig. 8, and zero in fig. 7. It is considerable for both W and Z in figs. 6 and 7, but small in fig. 8.

In these curves no correction has been introduced for any variation during an experiment of the temperature of the cells used as standards, for the error probably did not amount to more than two, or three, ten-thousandths of a volt, and there was some uncertainty as to such variations. The thermometer indicated the temperature of the water in the bath, but the standards being in boiling tubes were surrounded by air. It is, therefore, probable that they did not very readily follow any small variations in the temperature of the bath, and it was consequently thought best to introduce no correction.

In practice we seldom have to deal with such large changes of temperature as 10° C. produced in $2\frac{1}{2}$ hours. In order to observe whether lag existed with slow variations, an experiment was carried out, during which a change of about 2° up and down took place at the rate of 1° in fifty minutes, as shown in fig. 9. Since the corresponding change in E.M.F. was rather small, it seemed desirable in this case to introduce a correction for any change that might occur in the temperature of the standard cell. And, since, in consequence of the thin layer of air that separated this cell from the water in the bath, small changes in its temperature might not be accurately recorded by the thermometer in the water, an indirect method was employed for detecting any small changes in the E.M.F. of the standard by comparing it with the E.M.F.s of three cells placed in a water bath and frequently stirred. The standard was compared with these at short intervals during the experiment, and their temperature, which rose approximately through 0.54° , was carefully noted. One of these cells, although giving good results, did not appear to be quite as steady as the other two, viz., M and N, which were very consistent. It was accordingly discarded. Curves M and N connecting the E.M.F. differences of these cells with time are plotted in fig. 9. The dotted curve may be considered as their mean. The variation of this from the starting point, or from the base line *ab*, is due to two causes—(1) change in temperature of M and N, (2) change in the temperature of the standard. From the results obtained it may be fairly assumed that the cells M and N have not otherwise changed in themselves. If the variation due to change of temperature of M and N can be estimated, that due to change in the standards can then be deduced. But this cannot be done without assuming some knowledge of the quantity we are investigating, viz., taking it for granted that cells are readily affected by small changes of temperature. As, however, this conclusion is supported by much

FIG. 9.



evidence, it is probable that curves corrected by a quantity so obtained will be nearer the truth than if left uncorrected.

From previous experiments it appeared that the E.M.F. of M and N fell about 0.0010 volt per degree rise of temperature. The ordinates of the curve T_1 above the line cd give this rise of temperature from the beginning of the experiment, and are also numerically equal to the changes of E.M.F. Hence, if the ordinates of the dotted curve are diminished by these corresponding ordinates of T_1 , another curve ee is obtained, of which the ordinates from ab give the variation of the standard. Since it is wholly below ab , it follows that the E.M.F. of the standard fell during the experiment, but rose to nearly its old value at the conclusion, a result which agrees with the absolute measurements taken. This curve enables the figures obtained from the cells under test to be corrected, the correction, however, being small: they are given in their final form in fig. 9, along with the corresponding temperature curve T_2T_2 . The changes in E.M.F. were measured to 1/50,000th of a volt, and a larger scale is used in this diagram so as to render the differences more apparent. The curves are very similar to those already discussed. Lag is still evident, though of course much diminished. Cells W and Z show practically no lag of a semi-permanent character, but it is strongly marked in L and F, although a steady temperature had been maintained for some time at the end of the experiment. Curve L is noticeable, as showing the uncertain character of lag in a cell, a point which is also exemplified by the curve for B in fig. 8. Other curves of the same kind have been obtained, one of which relates to B, but they have not been reproduced.

It might be supposed that part of the lag observed was really due to lag in the thermometers themselves. But on subjecting these to cyclical changes of temperature this was found not to be the case.

In general, it thus appears that Clark cells of this type are very sensitive to changes of temperature, but are subject to a lag, which is variable in value, even when these changes of temperature are small. For that reason it is generally impossible to apply a correction which shall be accurate to 1/10,000th of a volt for even very slow variations of temperature. Of course, in work involving a knowledge of the absolute E.M.F. of the cell, this is of no great importance, as we do not know the value of the E.M.F. to greater accuracy than 0.1 per cent. in true volts, but it may be of importance when dealing with comparisons.

If we suppose a cell to be placed in a water bath, the temperature of which is 3.0° different from that of the cell previously, we may conclude that after the lapse of half an hour the lag will not amount to more than 0.1 per cent. of the E.M.F., and will generally be less. In such cases the temperature coefficient should be diminished some-

what in value when correcting for actual variations, unless these take place with extreme slowness. In fact, it would appear that a more suitable value for the temperature coefficient, for use under ordinary working conditions, would result from such curves as those given above, although it would not be the true value. It must, however, be remembered that cells differ among themselves somewhat as to the value of the coefficient.

The cells were carefully examined, but, although small differences were apparent, their appearance furnished no characteristics by which the observed phenomena might be accounted for. As already mentioned, the majority of the cells were constructed at the same time, and many were precisely alike as far as could be judged, for example, W, X, Z.

It has for some time past been suspected that the lag of the E.M.F. of a Clark cell behind the temperature was due not merely to the mean temperature of the cell itself lagging behind that of the bath, but to time being necessary for the variation of the amount of crystals in solution and for diffusion to take place.

How far this cause of lag is diminished by the use of the H type of cell, where there is only one horizontal surface of contact between metal and liquid, we are about to determine experimentally.

In conclusion, our thanks are due to Mr. W. G. Rhodes, as already stated, and also to several students, among whom we would mention Mr. F. S. Grogan, who gave much time to the work.

There appears to be a general tendency for the E.M.F. of cells set up in accordance with the final specification issued by the Board of Trade to fall somewhat below the normal value after the lapse of some months. For example, the E.M.F. of cells set up in October, 1894, although, as a rule, not differing from 1.434 volts at 15° C. by more than 1 part in 3000 when tested soon after construction, is now low by fully 1 part in 1000. The same may be said of cells set up in November, 1894. But the E.M.F. of cells constructed in June, 1895 although falling, is still not low by more than about 1 part in 2000.